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# New Aspects in Calorimetry

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Since the invention of the first isothermal ice-calorimeter [1] the development of calorimetric measuring systems has made rapid progress. The precision of recording calorific values has markedly improved. But the problem in calorimetry was and is that different measuring methods are permitted. Up to now two basic methods are globally recognized.

The most precise but also the most difficult measuring method is based upon an adiabatic testing conduct. In the ideal case there is no heat exchange between the calorimetric measuring cell and the ambience. For an evaluation of the combustion and calorific values this permits the simple application of the first main theorem of thermodynamics without the need for further mathematic corrections with the exception of sulfur and nitrogen corrections that have to be deducted from the total result.

$$H_0 = \frac{c_V \cdot \Delta T - Q_{\text{fremd}}}{m}$$

For a proper adiabatic test course, constructing the apparatus presents the main problem. So it is required for instance that the ambience of the calorific system follows up inertialessly the temperature of the inner vessel. This requires intelligent measuring and controlling circuits which consider precisely the complete time dependencies of the calorimetric process. Even smallest deviations from the adiabatic principle lead to result distortions not to be tolerated.

When adhering to the adiabatic principle and to the pertaining marginal conditions, then this calorimetric basic method represents by far the precisest procedure to determine combustion heats. Thus the adiabatic curve excels by optimum linearity especially when working with different calorimetric substances, and by the independence of the time courses in the dynamic process sections.

Beside the adiabatic basic method, also the isoperibolic measurement set-up has established itself. The advantages of this system are the easy apparatus set-up, as the ambience of the calorimeter just has to be maintained on constant, standard conditions.

From this results a relatively complex evaluation function which has to consider that during the static and dynamic phases of a calorimetric test, energy in form of heat will be exchanged with the ambience. Therefore the isoperibolic measuring method is based upon an energy balance which would be the result in case of an infinitely fast combustion. In order to reali-

ze these requirements which are impossible to accomplish in reality, a correction is added to the calculation basis, that is to the first main theorem. Acc. to DIN 51900 part 2 [2] this correction is given by using the Renault-Pfandler-equation. ISO 1928 [3] suggests, apart from this method, also to use the Dickinson correction.

This isoperibolic procedure involves that the determination of the combustion value of a substance is the direct consequence of the combination of thermodynamic facts and mathematical corrections. This limits substantially the linear range of a calorimeter on the one hand, but the result depends on the other hand directly on the combustion course and the combustion time of the sample. If these caloric parameters differ essentially between the chosen standard and the sample to be determined, one can expect a result that is constant but constantly deviating. Furthermore, the isoperibolic method also does not offer any considerable advantages with respect to time, as DIN, ISO, BSI and ASTM-standards [4] require for this calori-

## KEYWORDS

Adiabatic and isoperibolic method,  
DIN 51900 part 2/ISO 1928/ASTM  
240d/BSI, cooling unit independent  
on water, oxygen decomposition,  
automatic handling



Ill. 1: The Authors Hubert Pinhack and Andreas Reichert with the calorimeter

metric method a pretest time of at least 5 minutes, a main test time of up to 10 minutes and an after test time of also at least 5 minutes. These times are the direct result of the necessity to achieve stable results as these are the basis for a precise determination of combustion and calorific values. Implemented measurement time reductions do lead to a gain in time, but also go together with reduced precision and linearity. Especially if there are deviations in the combustion course of the sample from that of the standard, errors are unavoidable. These error sources are less represented by the standard deviation of individual test series but more so by the absolute deviation of the actual calorific value.

In the new calorimeter generation (Ill. 1) special attention is paid to this problem. Here an optimum of method flexibility plays a decisive part. The justified demand of the users for quicker detection systems has to be considered just as well as the conformity of the measuring results with globally accepted standards. It can be observed in how far an existing calorimetric system can also represent an analytical problem solution for other jobs (e.g. sample decomposition of complex organic matrices) and contains thus an analytic and simultaneous preparative part.

### Free Choice of Methods

The globalisation of economy involves that there are different philosophies with respect to the mentioned basic calorimetric procedures. Due to domestic manufacturers, measurements in the United States of America are mostly carried out isoperibolically while in Europe adiabatic measurements procedures have been established. Basically one should think that both determination methods will lead to the same results, whereby a comparability of up to 300 J is permitted according to DIN; ISO or ASTM: If, for instance, coal has been mined in South Africa and the calorific value is determined isoperibolically, then the control measurements should be carried out according to the same procedure for a better comparability. Therefore the user should either have two calorimeters at his place or select a system that offers the possibility to apply as well adiabatic as also isoperibolic basic procedures. As most important result support and as a safety measure for the user, these measurements should be carried out precisely according to DIN, ISO; BSO or ASTM.

A justified demand of the users was and is the development of a calorimeter which beside analytical precision and standard

conformity also ensures a high sample throughput. But these requirements of a calorimetric system are a contradiction in themselves as all known world standards require a certain measurement time. Presently isoperibolic systems are offered which meet the requirements of a shorter measuring period due to a mathematic shortening of the time of measurement, but they do not correspond with calorimetric standards. A worsening of linearity has to be taken into account as well. So here would be a possibility to introduce a time reduced basic method beside the validated methods. Thus a measurement in rapid test sequence would be possible for unofficial jobs and for samples with known combustion behaviour. By reversing the basic method, reliable and standardized tests can be carried out according to adiabatic or isoperibolic procedures in addition.

### Economy of a Calorimeter

Beside the analytical precision and the adherence to standardized measuring procedures, the economy of a calorimeter is of importance. Among the most intensive operating costs are apart from the operating personnel consumption materials such as oxygen or water as well as space requirements in the laboratory. In order to keep operating expenditures as low as possible, a calorimeter has to work off automatically all time consuming and error involving working steps. Among these are especially the automatic water handling for an exact filling of the inner vessel, an automatic pressurizing and degassing device as well as a completely autarkical control circuit for a defined setting of the operating parameters. The value of an analytical system also depends on the issue whether other laboratory jobs can be simultaneously processed with it. Thus the calorimeters partly ensure a simultaneous sample decomposition in the halogen and sulfur determination.

The newest calorimeter generation of Messrs. IKA-Analysentechnik disposes of a technology that corresponds with all the described requirements of such a system. The basic method can be optionally selected, thus an adiabatic or isoperibolic mode of operation can be set. The procedure strictly adheres to the valid world standards DIN 51900, ASTM 240 d, ISO 1928 etc. in view of test set-up, performance and documentation. A dynamic method permits time reduced measurements. This versatility of methods within one instrument permits the flexible processing of different samples, whereby an optimum adaptation to corresponding referen-

ce systems is given. Beside the optional selection of the basic method, the first "dry" cooler as well as an automatic water-handling-system (Ill. 2) are used in calorimetry. Apart from a compact instru-



Ill. 2: IKA C 5000 with dry cooling system



Ill. 3: Decomposition vessel

ment set-up without any further peripheries, a complete independence from the water mains is given and a maintenance-free cooling is possible. Economy and productivity are ensured by the optional use of special decomposition vessels. Thus it was demonstrated by several working groups that when using special AOD-decomposition vessels with catalytically activated coatings (Ill. 3), a quantitative decomposition of organic substances or of organically contaminated inorganic samples for a simultaneous halogen, phosphate, nitrogen, mercury and sulfur determination is possible [5, 6, 7]. It could be shown here that even with materials containing bromine and iodine, retrieval rates of 97–100% were achieved. These outstanding decomposition results were mainly due to the combination of good thermodynamic conditions in such a decomposition vessel ( $T = 1500\text{ }^{\circ}\text{C}$  in the core,  $T_{\text{gas}} 500\text{--}600\text{ }^{\circ}\text{C}$ ;  $p = 150\text{--}250$  bar) with specific catalysts, which led in case of sulfur analytics to a complete (100%) formation of  $\text{SO}_3$ , and in halogen analytics the generating of elementary halogens was prevented.

For a further increase in productivity, the calorimeter system can be enlarged by a sampler. By serial communication with the main computer of the calorimeter, samples can be managed and controlled and worked off without mix-up.